

United States Patent [19]

Connell et al.

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[45] Date of Patent: Nov. 19, 1991

[54] POLYIMIDAZOLES VIA AROMATIC NUCLEOPHILIC DISPLACEMENT

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[73] Assignee: The United States of America as represented by the Administrator of the National Aeronautics and Space Administration, Washington, D.C.

[21] Appl. No.: 508,316

[22] Filed: Apr. 12, 1990

[51] Int. Cl.⁵ C07F 9/28; C07D 211/70; C07D 211/82

[52] U.S. Cl. 548/119; 548/336; 548/337; 548/342

[58] Field of Search 548/337, 342, 119, 336

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PUBLICATIONS

Radlmann et al., Chem. Abstracts, vol. 75, No. 26, 152165u.

Kuenzel et al., Chem. Abstracts., vol. 72, No 4, 68047n. Farberfabriken, Chem. Abstracts, vol. 72, No. 12, 56103q.

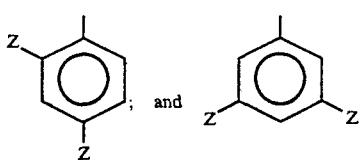
Primary Examiner—Johann Richter
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[57] ABSTRACT

Polyimidazoles (PI) are prepared by the aromatic nucleophilic displacement reaction of di(hydroxyphenyl)imidazole monomers with activated aromatic dihalides or activated aromatic dinitro compounds. The reactions are carried out in polar aprotic solvents such as N,N-dimethylacetamide, sulfolane, N-methylpyrrolidinone, dimethylsulfoxide, or diphenylsulfone using alkali metal bases such as potassium carbonate at elevated temperature under nitrogen. The di(hydroxyphenyl)imidazole monomers are prepared by reacting an aromatic aldehyde with a dimethoxybenzil or by reacting an aromatic dialdehyde with a methoxybenzil in the presence of ammonium acetate. The di(methoxyphenyl)imidazole is subsequently treated with aqueous hydrobromic acid to give the di(hydroxyphenyl)imidazole monomer. This synthetic route has provided high molecular weight PI of new chemical structure, is economically and synthetically more favorable than other routes, and allows for facile chemical structure variation due to the availability of a large variety of activated aromatic dihalides and dinitro compounds.

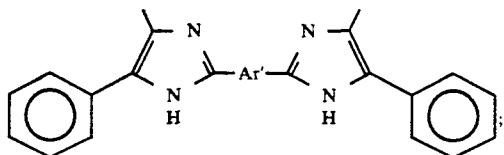
8 Claims, No Drawings

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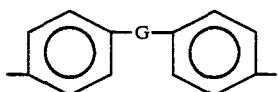
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wherein Z is a radical selected from the group consisting of: CF_3 , F, Cl, Br, I, CH_3 , OCH_3 , CH_2CH_3 , NO_2 , and Ph; and

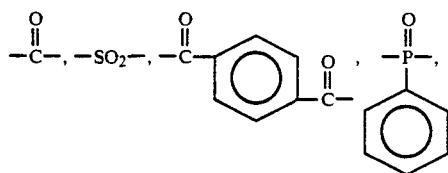


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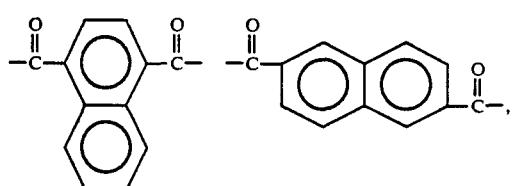
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wherein Ar' is selected from the group consisting of:

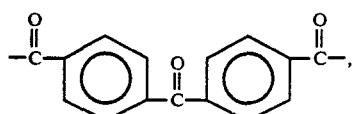
wherein G is not a substituent or is a substituent selected from the group consisting of: CH_2 , O, S, $\text{C}=\text{O}$, and SO_2 ; wherein X is a radical selected from the group consisting of:



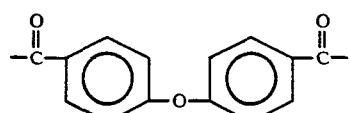
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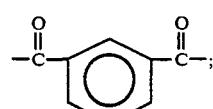
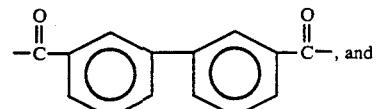
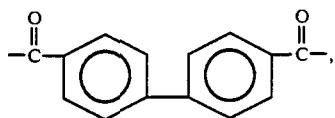
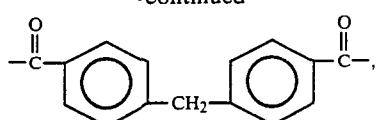


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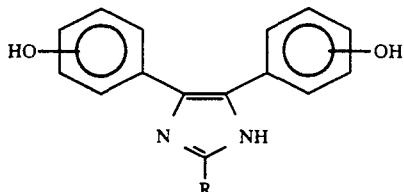
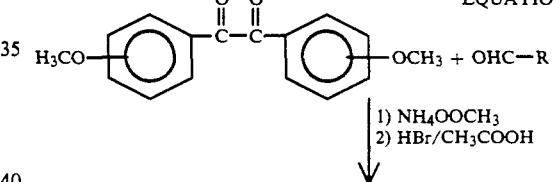
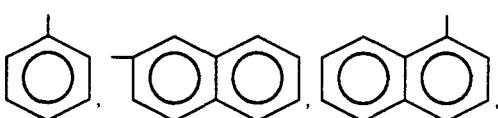
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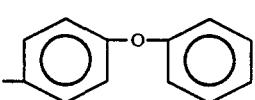
25 and wherein n is an integer between 4 and 100.

The synthesis of PI involved the use of di(hydroxyphenyl)imidazole monomers of two different types; those prepared from monoaldehydes as shown in Equation (1), and those prepared from dialdehydes as depicted in Equation (2).

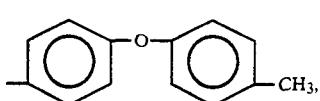
EQUATION (1)

50 where R can be H, CH_2CH_3 , OCH_3 , CH_3 , CF_3 ,

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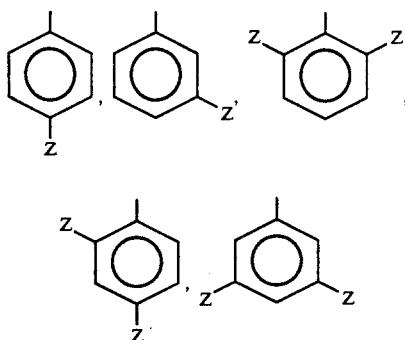


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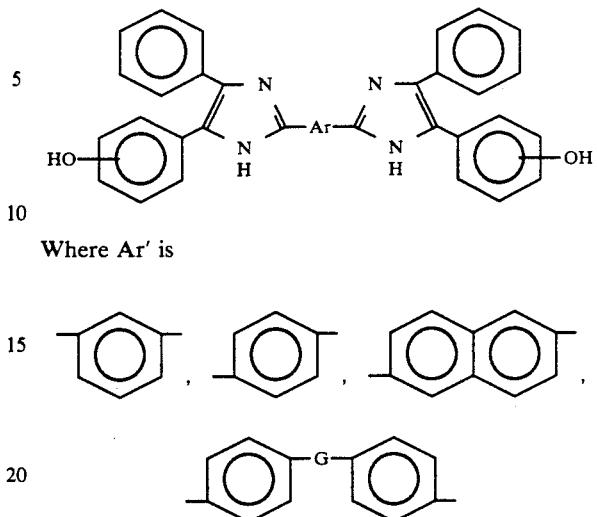


where Z can be CH_3 , CF_3 , OCH_3 , Ph , NO_2 , I , Cl , Br , F , and CH_2CH_3 . The catenation of the hydroxy group may be meta meta, para para, or meta para.

The general reaction sequence for the preparation of 20 the di(hydroxyphenyl)imidazoles prepared from dialdehydes is represented in Equation (2).

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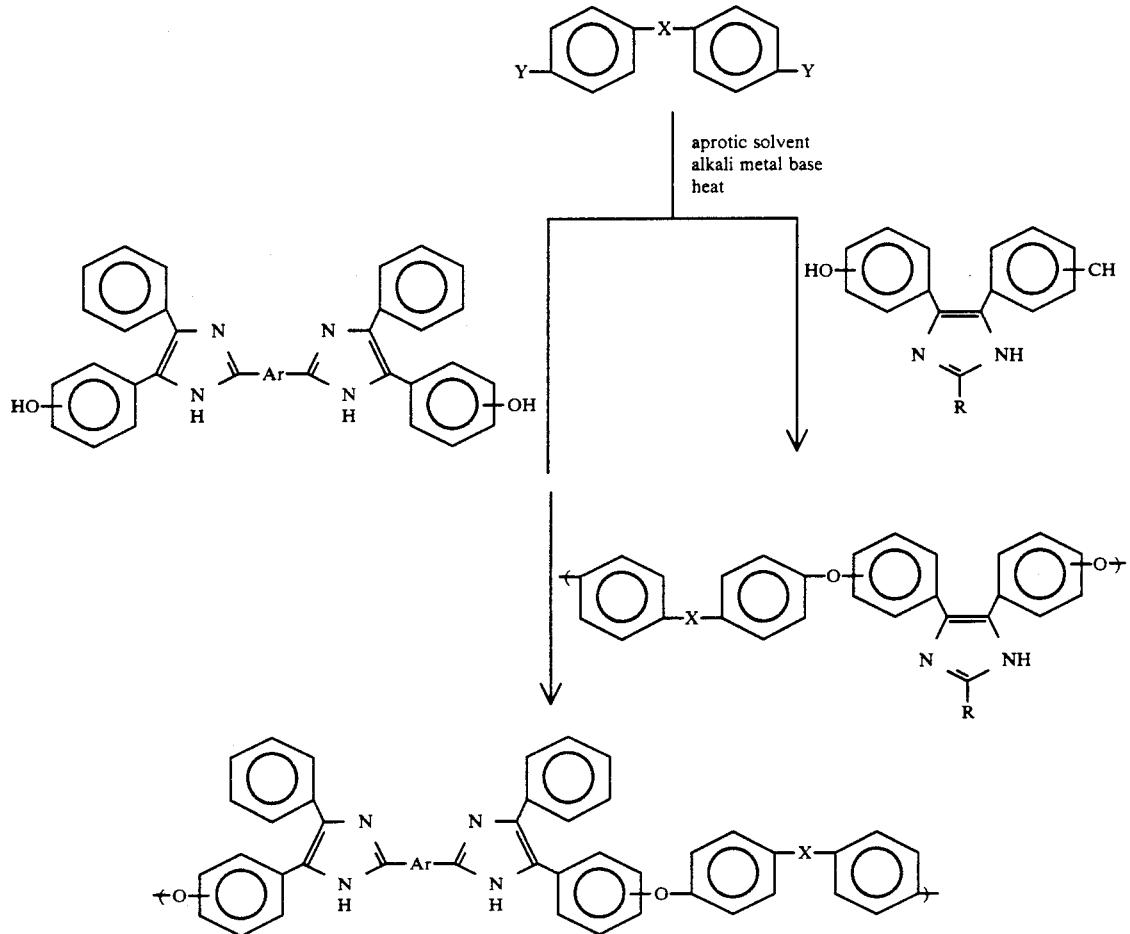
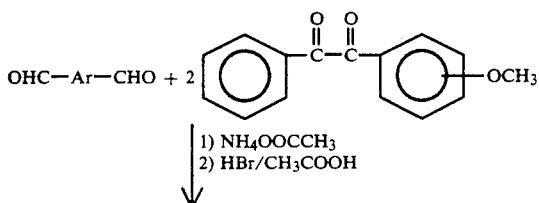
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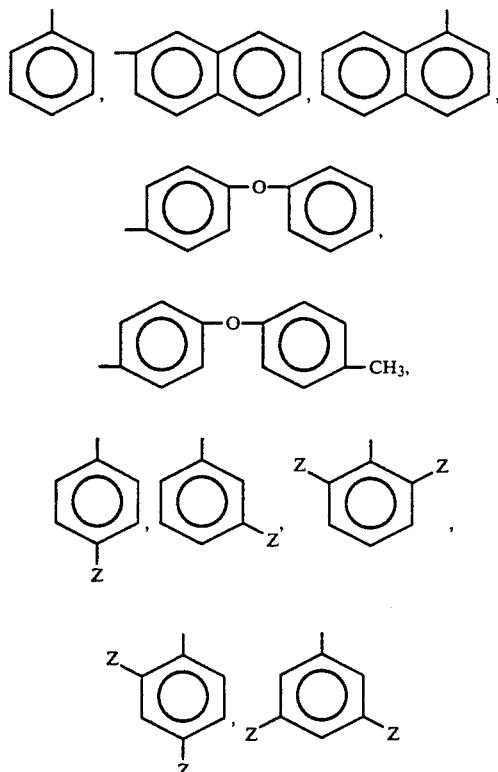
Where G is nil, CH_2 , O, S, $\text{C}=\text{O}$, SO_2 .

The catenation of the hydroxy group may be meta meta, para para or meta para.

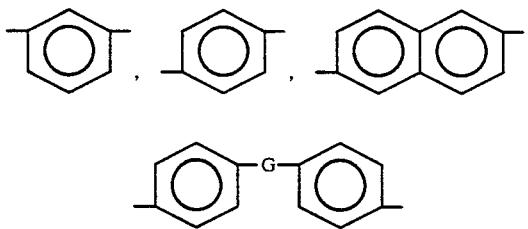
The general reaction sequence for the synthesis of PI is represented below:



Where Y can be Cl, F, or NO₂
where R can be H, CH₃, CH₂CH₃, OCH₃, CF₃

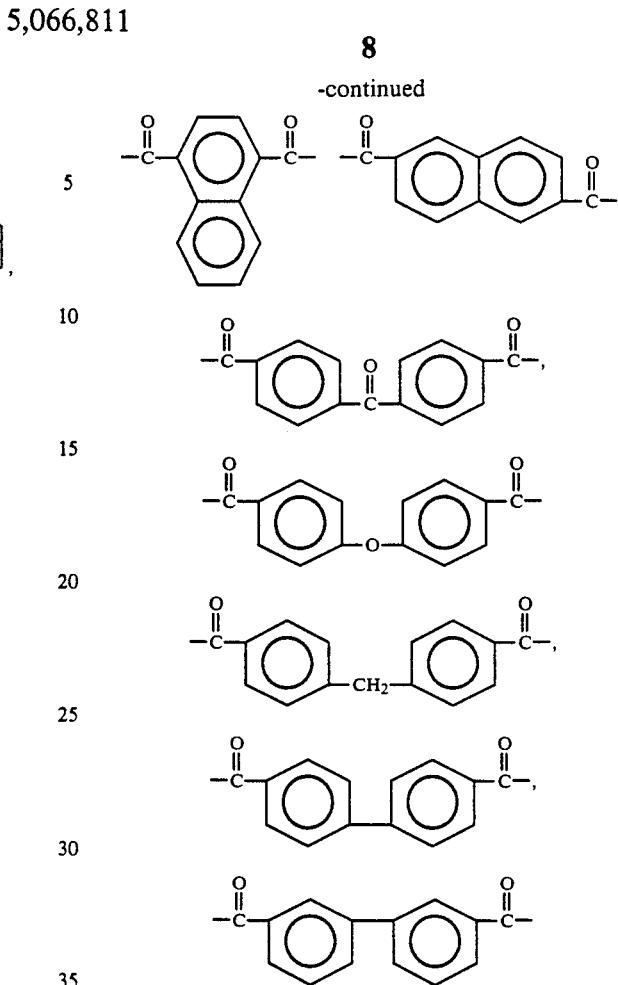
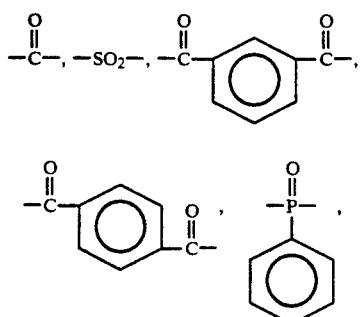


Where Z can be CH₃, CF₃, OCH₃, Ph, NO₂, I, Cl, Br, F, CH₂CH₃, etc.
Where Ar' can be



Where G can be nil, CH₂, O, S, C=O, SO₂.

The substitution of the hydroxy group may be meta, para para, or meta para, and X can be



DESCRIPTION OF THE PREFERRED EMBODIMENTS

40 Having generally described the invention, a more complete understanding thereof can be obtained by reference to the following specific examples which are provided herein for purposes of illustration only and do not limit the invention.

EXAMPLES

Example 1

The following example illustrates the reaction sequence for the synthesis of a polyimidazole where R is a phenyl group and X is terephthaloyl and Y is F (see Equation (3)).

Monomer Synthesis

4,5-Bis(4-hydroxyphenyl)-2-phenylimidazole

55 Into a one liter three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet and reflux condenser was placed 4,4'-dimethoxybenzil (13.53 g, 0.05 mol) and acetic acid (300 ml).

60 The mixture was stirred with heating to give a yellow solution. Ammonium acetate (68.0 g, 0.88 mol) and benzaldehyde (26.0 g, 0.25 mol) were added along with additional acetic acid (100 ml). The solution was heated to reflux (about 120° C.) overnight under nitrogen. The

65 orange solution was cooled and poured into water to give an off-white precipitate which was collected, washed repeatedly with water and dried at 125° C. Yield was 17.5 g (98%) of white solid. Recrystallization

from ethanol/water (3:1) gave 15.8 g (89%) of white crystals, m.p. 198°–200° C.

4,5-Bis(4-methoxyphenyl)-2-phenylimidazole (15.8 g, 0.044 mol) was placed in a 250 ml three neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, reflux condenser and hydrogen bromide gas trap along with acetic acid (75 ml) and 47–49% aqueous hydrogen bromide solution (130 ml). The mixture was heated to reflux for 16 hours, cooled, 10 poured into water to give a white solid, which was neutralized with sodium hydroxide, collected, washed with water and dried at 100° C. Yield was 13.7 g of white solid. Recrystallization from ethanol/water (3:1) 15 gave 11.5 g (79%) of white crystals, m.p. 327°–330° C. Anal. Calcd. for $C_{21}H_{16}N_2O_2$: C, 76.80%; H, 4.91%; N, 8.53%. Found: C, 76.50%; H, 5.00%; N, 8.44%.

Polyimidazole Synthesis

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, moisture trap and reflux condenser was placed 4,5-bis(4-hydroxyphenyl)-2-phenylimidazole (2.4267 g, 7.5 mmol), 1,4-bis(4-fluorobenzoyl)benzene (2.4173 g, 7.5 mmol), pulverized anhydrous potassium carbonate (2.4 g, 17.0 mmol, 15% excess), dry N,N-dimethylacetamide (DMAc) (20 ml, 20% solids) and toluene (30 ml). The mixture was heated to about 135° C. for four hours and then heated to 155° C. overnight under nitrogen. The viscous dark red solution was diluted with DMAc (20 ml) and precipitated into water/acetic acid mixture, collected, washed successively in water and methanol and dried at 125° C. Yield was 4.4 g (97%) of yellow polymer with a glass transition temperature of 248° C. The inherent viscosity of a 0.5% solution in DMAc at 25° C. was 0.89 dL/g. Thin films cast from DMAc 40 solution gave tensile strength, tensile modulus and elongation at 25° C. of 14,200 psi, 407,000 psi and 6.0%; at 177° C. of 8,200 psi, 306,000 psi and 6.0%; and at 200° C. of 6,600 psi, 273,500 psi and 7.5%.

Example 2

The following example illustrates the reaction sequence for the synthesis of the polyimidazole where R is a phenyl group, X is a carbonyl group, and Y is F (see 50 Equation (3)).

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, moisture trap and reflux condenser was placed 4,5-bis(4-hydroxyphenyl)-2-phenylimidazole (3.2836 g, 10.0 mmol), 4,4-difluorobenzophenone (2.1819 g, 10.0 mmol), pulverized anhydrous potassium carbonate (3.2 g, 23.0 mmol, 15% excess), dry DMAc (22 ml, 20% solids) and toluene (35 ml). The mixture was heated to 55 about 135° C. for four hours and then heated to 155° C. overnight under nitrogen. The viscous dark red solution was diluted with DMAc (20 ml) and precipitated into water/acetic acid mixture, collected, washed successively in water and methanol and dried at 125° C. Yield was 4.04 g (97%) of yellow polymer with a glass transition temperature of 273° C. The inherent viscosity of a 0.5% solution in DMAc at 25° C. was 1.38 dL/g. Thin films cast from m-cresol solution gave tensile strength, tensile modulus and elongation at 25° C. of 17,600 psi, 464,000 psi and 8.1%, at 93° C. of 15,300 psi, 402,000 psi and 5.6% and at 232° C. of 7400 psi, 285,300 psi and 4.8% respectively.

a 0.5% solution in DMAc at 25° C. was 0.61 dL/g. Thin films cast from DMAc solution gave tensile strength, tensile modulus and elongation at 25° C. of 13,300 psi, 405,200 psi and 5.0% and at 177° C. of 9,500 psi, 400,500 psi and 3.4% respectively.

Example 3

The following example illustrates the reaction sequence for the synthesis of the polyimidazole where Ar' is 1,4-phenylene, X is isophthaloyl and Y is F (See Equation 3).

Monomer Synthesis

1,4-Bis[2-imidazolyl-4-(4-hydroxyphenyl)-5-(phenyl)]-benzene

Into a 500 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet and reflux condenser was placed 4-hydroxybenzil (9.05 g, 0.04 mol) and acetic acid (100 ml). The mixture was stirred with heating to give a yellow solution. Terephthalaldehyde (2.68 g, 0.02 mol) was subsequently added along with ammonium acetate (43.1 g, 0.56 mol) and acetic acid (50 ml). The mixture was stirred with heating and within one hour a yellow precipitate formed. The mixture was then heated to reflux (about 120° C.) for six hours. The mixture was cooled and poured into ice water, and the yellow solid collected, washed with water, and dried at 100° C. Yield was 10.7 g (98%). The solid was recrystallized from N,N-dimethylformamide (100 ml) and water (25 ml) using activated charcoal to give 8.6 g (79%) of yellow solid, m.p. about 390° C. Anal. Calcd. for $C_{36}H_{26}N_4O_2$: C, 79.10%; H, 4.79%; N, 10.25%. Found: C, 78.81%; H, 4.87%; N, 10.12%.

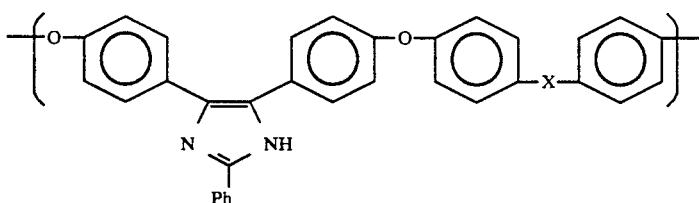
Polyimidazole Synthesis

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, moisture trap and reflux condenser was placed 1,4-bis[2-imidazolyl-4-(4-hydroxyphenyl)-5-(phenyl)]benzene (2.7330 g, 0.005 mol), 1,3-bis(4-fluorobenzoyl)benzene (1.6115 g, 0.005 mol), pulverized anhydrous potassium carbonate (1.6 g, 0.0115 mol, 15% excess), dry DMAc (18 ml, 18% solids) and toluene (25 ml). The mixture was heated to about 135° C. for four hours, and then heated to 155° C. overnight under nitrogen. The viscous dark red solution was diluted with DMAc (20 ml) and precipitated into water/acetic acid mixture, collected, washed successively in water and methanol and dried at 60 125° C. Yield was 4.04 g (97%) of yellow polymer with a glass transition temperature of 273° C. The inherent viscosity of a 0.5% solution in DMAc at 25° C. was 1.38 dL/g. Thin films cast from m-cresol solution gave tensile strength, tensile modulus and elongation at 25° C. of 17,600 psi, 464,000 psi and 8.1%, at 93° C. of 15,300 psi, 402,000 psi and 5.6% and at 232° C. of 7400 psi, 285,300 psi and 4.8% respectively.

Polymer characterization is presented in Table 1, and thin film and adhesive properties are presented in Table 2 and Table 3, respectively.

TABLE 1

POLYMER CHARACTERIZATION



POLYMER	X	INHERENT ¹ VISCOOSITY, dL/g	GLASS TRANSITION ² TEMPERATURE, °C.
P1		0.24	318
P2		0.41	277
P3		0.61	259
P4		0.53	258
P5		0.40	248
P6		0.89	248
P7		0.49	239
P8		0.58	231
P9		0.64	230
P10		0.55	230

TABLE 2

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POLY- MER	THIN FILM PROPERTIES ¹			
	TEST TEMP., °C.	TENSILE STRENGTH, KSI	TENSILE MODULUS, KSI	ELONG., %
P3	25	13.3	405.2	5.0
	177	9.5	400.0	3.4
P6	25	14.2	407.0	6.0
	177	8.2	306.0	6.0
	200	6.6	273.0	7.5

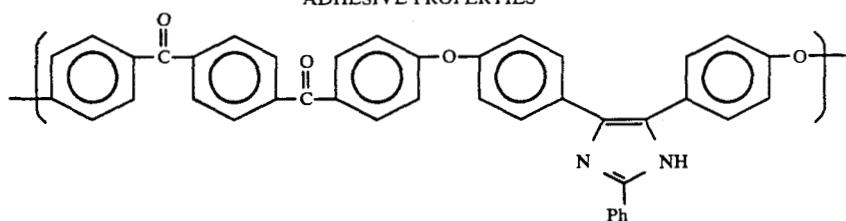
TABLE 2-continued

POLY- MER	THIN FILM PROPERTIES ¹			
	TEST TEMP., °C.	TENSILE STRENGTH, KSI	TENSILE MODULUS, KSI	ELONG., %
P7	25	13.8	390.0	6.3
	177	8.4	285.0	6.2
P10	25	12.0	362.4	4.0
	177	8.3	336.4	3.8

¹Tested according to ASTM D882, average of four specimens per test condition.

TABLE 3

ADHESIVE PROPERTIES*

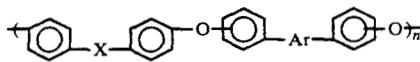


BONDING CONDITIONS	TEST TEMP., °C.	TI/TI TENSILE SHEAR STRENGTH, PSI	FAILURE MODE
300° C., 100 PSI, 1 HR	25	4660	50% COHESIVE
300° C., 500 PSI, 1 HR	25	4120	20% COHESIVE
300° C., 200 PSI, 1 HR	25	4810	75% COHESIVE
"	93	3800	30% COHESIVE
"	177	3700	40% COHESIVE
"	200	3050	45% COHESIVE

*Tested according to ASTM D1002, average of four specimens per test. Inherent viscosity of polymer 0.57 dL/g, glass transition temperature 245° C.

What is new and desired to be secured by letters patent of the United States is:

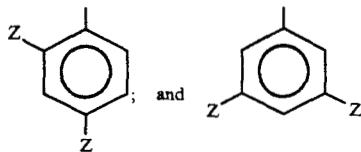
1. A polyimidazole having the general structural formula:



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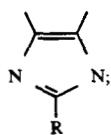
wherein the substitution of oxygen is selected from the group consisting of meta, meta, para, para, and para meta; wherein Ar is a radical selected from the group consisting of:

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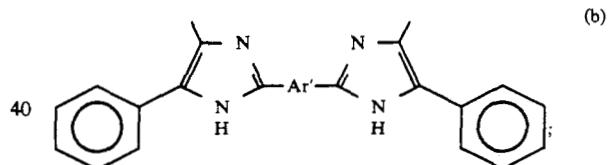


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wherein Z is a radical selected from the group consisting of: CF₃, F, Cl, Br, I, CH₃, OCH₃, CH₂CH₃, NO₂, and Ph; and



(a)

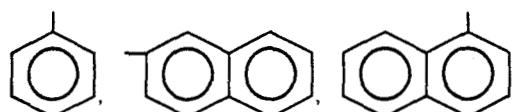


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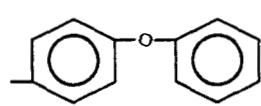
wherein R is selected from the group consisting of: H, CH₃, CF₃, CH₂CH₃, OCH₃,

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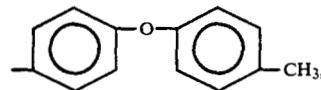
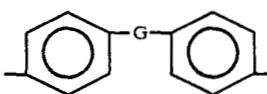
wherein Ar' is selected from the group consisting of:



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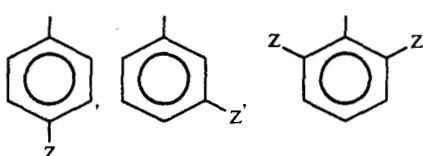


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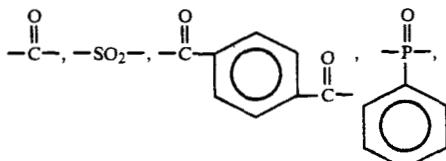


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wherein G is a bond or is a substituent selected from the group consisting of: CH₂, O, S, C=O, and SO₂; wherein X is a radical selected from the group consisting of:

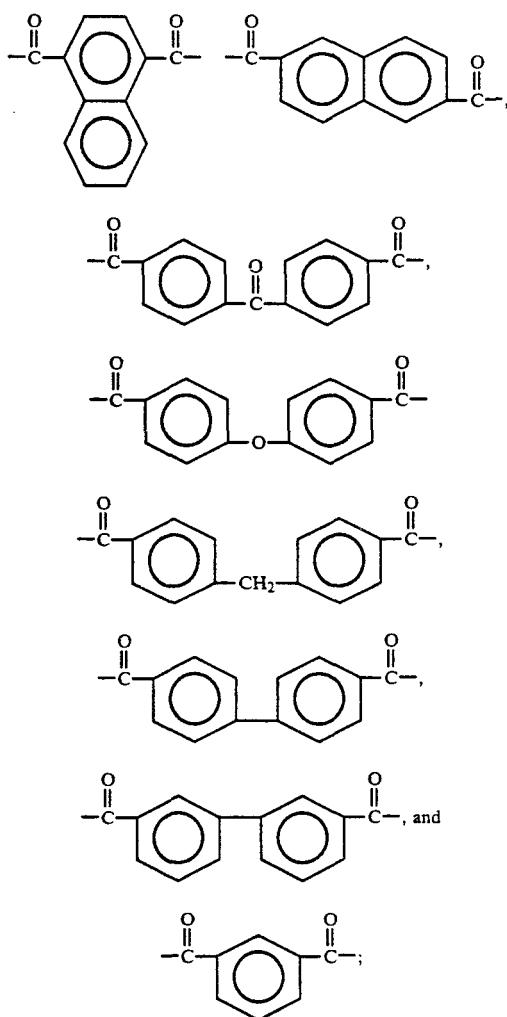


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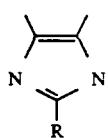
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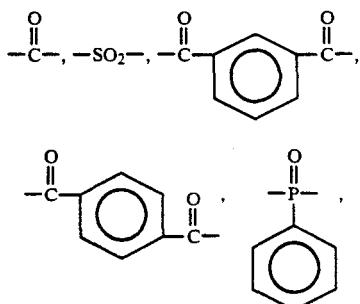
and wherein n is an integer between 4 and 100.

2. The polyimidazole of claim 1, wherein Ar is a radical of the structure:



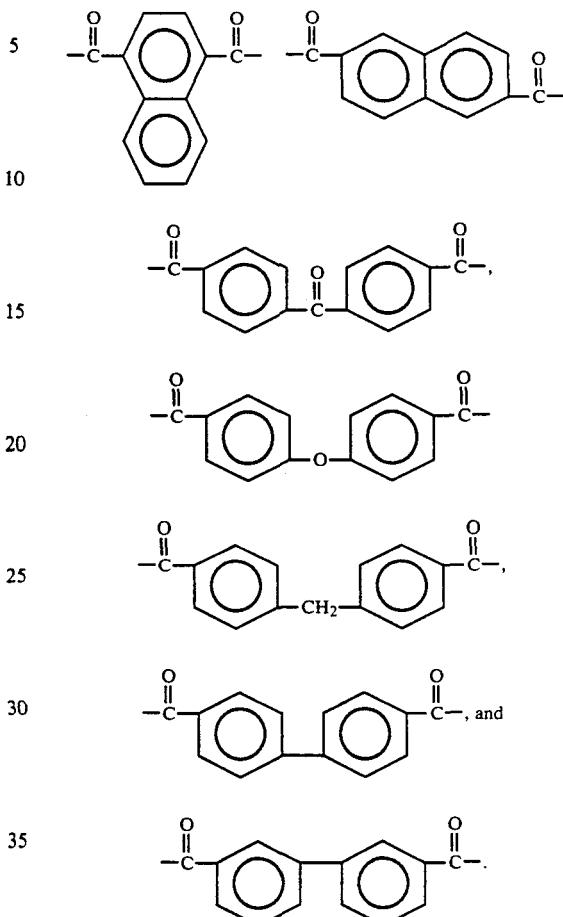
and wherein R is a phenyl group.

3. The polyimidazole of claim 2, wherein X is selected from the group consisting of:

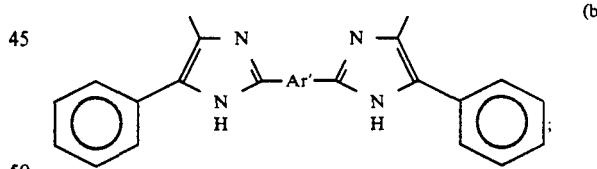


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40 4. The polyimidazole of claim 1, wherein Ar is a radical of the structure:



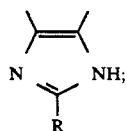
and wherein Ar' is 1,4-phenylene.

5. The polyimidazole of claim 4, wherein X is isophthaloyl.

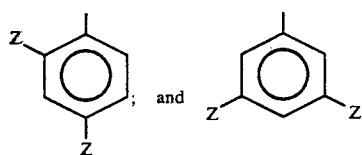
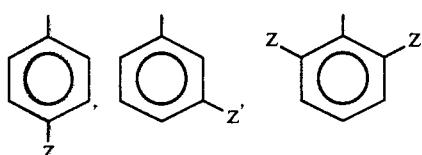
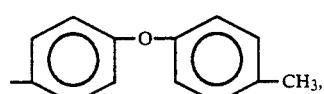
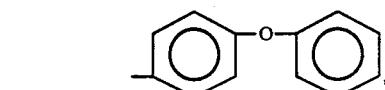
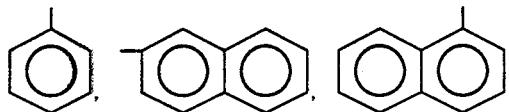
55 6. A di(hydroxyphenyl)imidazole having the general structure:



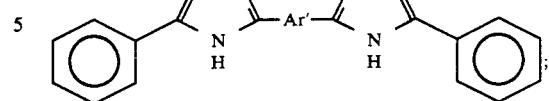
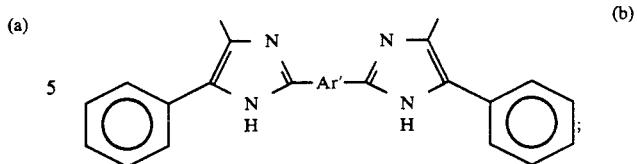
65 wherein the catenation of the hydroxy radicals is selected from the group consisting of meta meta, para para, or para meta; wherein Ar is selected from the group consisting of:



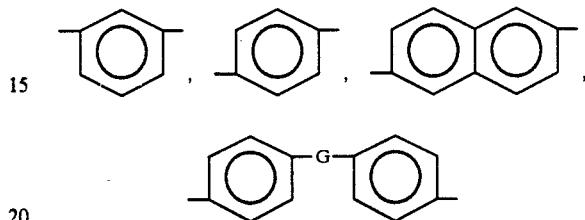
wherein **R** is selected from the group consisting of: H,
10 **CF**₃, **CH**₃, **CH**₂**CH**₃, **OCH**₃,



wherein **Z** is a radical selected from the group consisting of: **CF**₃, **F**, **Cl**, **Br**, **I**, **CH**₃, **OCH**₃, **CH**₂**CH**₃, **NO**₂,
45 and **Ph**; and
and **Ph**; and

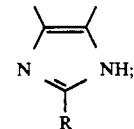


wherein **Ar'** is selected from the group consisting of:



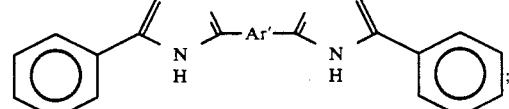
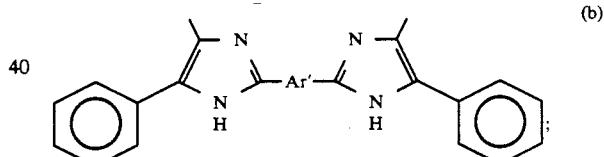
and wherein **G** is a bond or is a substituent selected from the group consisting of: **CH**₂, **O**, **S**, **C=O**, and **SO**₂.

7. The di(hydroxyphenyl)imidazole of claim 6,
25 wherein **Ar** has the general structure:



and wherein **R** is a phenyl group.

35 8. The di(hydroxyphenyl)imidazole of claim 6,
wherein **Ar** has the general structure:



and wherein **Ar'** is 1,4-phenylene.

* * * * *